DSCR

DLA's Lead Center For Aviation Support

ENVIRONMENTAL RESTORATION PROGRAM

# Natural Attenuation of Chlorinated Solvents

## A DSCR Restoration Advisory Board (RAB) Technical Training Session

Presented by
Mitretek Systems

**April 11, 2005**

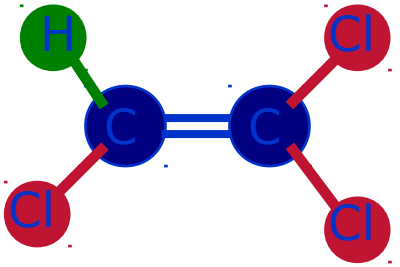
# Briefing Overview

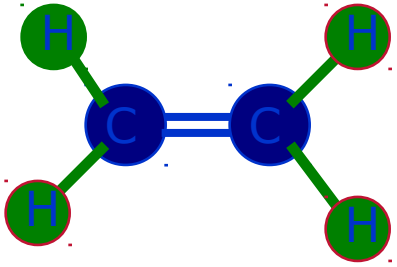
- What are chlorinated solvents?
- Why should we care about them?
- Solvent cleanup challenges
- Natural attenuation solvent cleanup solutions
- What is reductive dechlorination?
- How does reductive dechlorination work?
- Pros and cons of natural attenuation for chlorinated solvent remediation

# What are Chlorinated Solvents?

- **Synthetic organic hydrocarbons in which one or more hydrogen atoms have been replaced by chlorine atoms (a.k.a. chlorinated volatile organic compounds – CVOCs)**

TCE can be “parent” solvent or a reductive dechlorination “daughter” of PCE



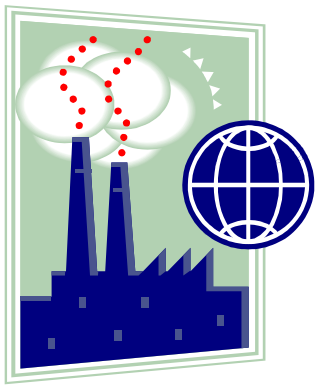

Ethene is a fully dechlorinated, non-toxic “daughter” of chlorinated ethenes

# Common Chlorinated Hydrocarbons

- **Chlorinated ethenes (2 carbon atoms, plus…)**
  - **PCE – Tetrachloroethene (4 Cl atoms, no H atoms)**
  - **TCE – Trichloroethene (3 Cl atoms, 1 H atom)**
  - **DCE – Dichloroethene (2 Cl atoms, 2 H atoms)**
  - **VC – Vinyl Chloride (1 Cl atom, 3 H atoms)**
- **Chlorinated ethanes (2 carbon atoms, plus…)**
  - **PCA – (4 Cl atoms, 2 H atoms)**
  - **TCA – (3 CL atoms, 3 H atoms)**
  - **DCA – (2 CL atoms, 4 H atoms)**
- **Other examples**
  - **Carbon Tetrachloride, Chloroform**

# Where Do They Come From?

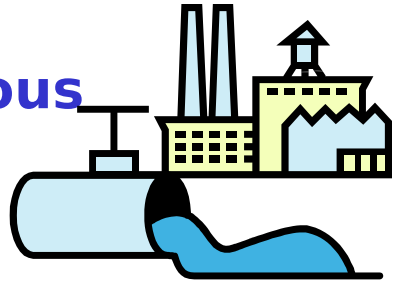
- **Chlorinated solvents (CVOCs) are commonly used as:**
  - **Industrial degreasers**
  - **Dry-cleaning agents**
  - **Septic system cleaners**
  - **Solvents to dissolve other substances (glue, paint)**
  - **Pesticide ingredients**
- **In common household products**
  - **Drain cleaners, printing inks, spot cleaners, stain repellents, shoe polishes, glues, and aerosol sprays**



# Why Do We Care About Them?

- **CVOCs are persistent dense non-aqueous-phase liquids (DNAPLs) – more about that later**
- **CVOCs have varying degrees of toxicity**
- **Possible human exposure routes:**
  - **Direct contact (e.g., absorption through skin)**
  - **Ingestion (e.g., eating or drinking contaminated substance)**
  - **Inhalation (e.g., breathing CVOC vapors)**

# Why Are They in the Environment?



- **CVOCs were not regulated as hazardous substances until the late 1970s**
- **Historically, CVOCs were commonly disposed of on the ground surface or in unlined waste disposal pits/landfills**
- **Once released, solvents tend to move downward through soil – often into groundwater**
- **Dissolved solvent constituents can be carried far from their release points in groundwater**

# Solvent Cleanup Challenges: The Bad News ☹

- **DNAPLs, which are the source of CVOCs:**
  - **Move with gravity rather than with groundwater flow**
  - **Tend to move in “blobs”**
  - **Bind to clay minerals**
  - **Dissolve very slowly into groundwater**
  - **Volatilize as vapors**
  - **Are subject to low groundwater cleanup criteria**

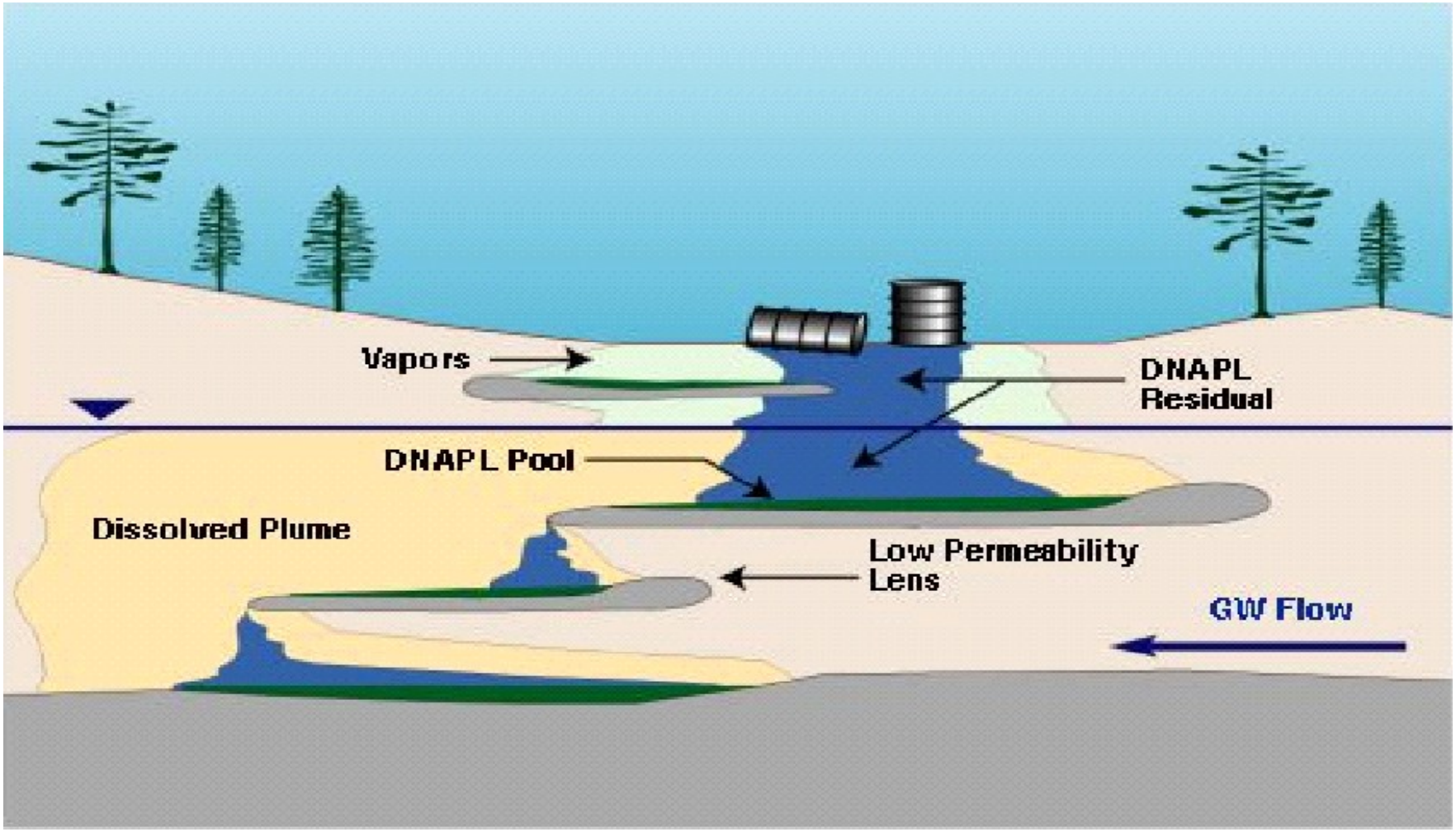
# Solvent Cleanup Challenges: The Bad News ☹

**Therefore, DNAPLs**

- **Are difficult to fully characterize in the subsurface**
- **Persist in the environment for very long times**
- **Act as long-term sources for groundwater and vapor contamination**
- **Pose significant remediation challenges for currently available engineered cleanup technologies**
- ***Few, if any, DNAPL sites have been fully restored after 25+ years of cleanup***

***DNAPLs are stubborn!***

# Conceptual DNAPL Site Model



# Solvent Cleanup Solutions: The Good News ☺

- **If receptors are not exposed to CVOC contaminants, there is no health risk**
- **"Mother Nature" has an effective CVOC remediation tool kit we can use:**

***Natural Attenuation!***

- **Natural attenuation of CVOCs occurs when any of several mechanisms act to reduce contaminant volume, mobility, or toxicity**

# Ma Nature's Tool Kit

## Natural Attenuation Mechanisms

- Physical mechanisms
  - Dilution/dispersion
  - Sorption
  - Volatilization
- Chemical (abiotic) mechanisms
  - Oxidation
  - Mineralization
- Biological mechanisms
  - Reductive dechlorination
  - Co-metabolism

# Solvent Cleanup Solutions: The Good News ☺

- **Under the right subsurface site conditions**
  - **Natural mineral reactions can transform CVOCs into harmless chemicals**
  - **Subsurface bacteria can actually "consume" the chlorine atoms in CVOCs, resulting in reductive dechlorination**
  - **Physical process can reduce CVOC concentrations in groundwater and control plume migration**

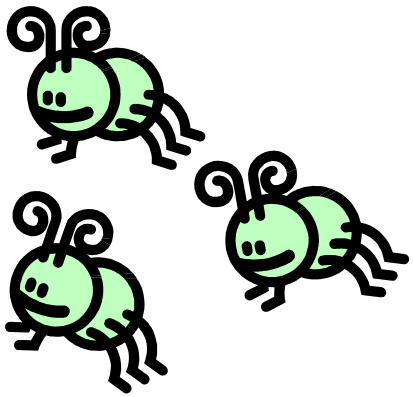
***Mother Nature can Help!***

# What is Reductive Dechlorination?

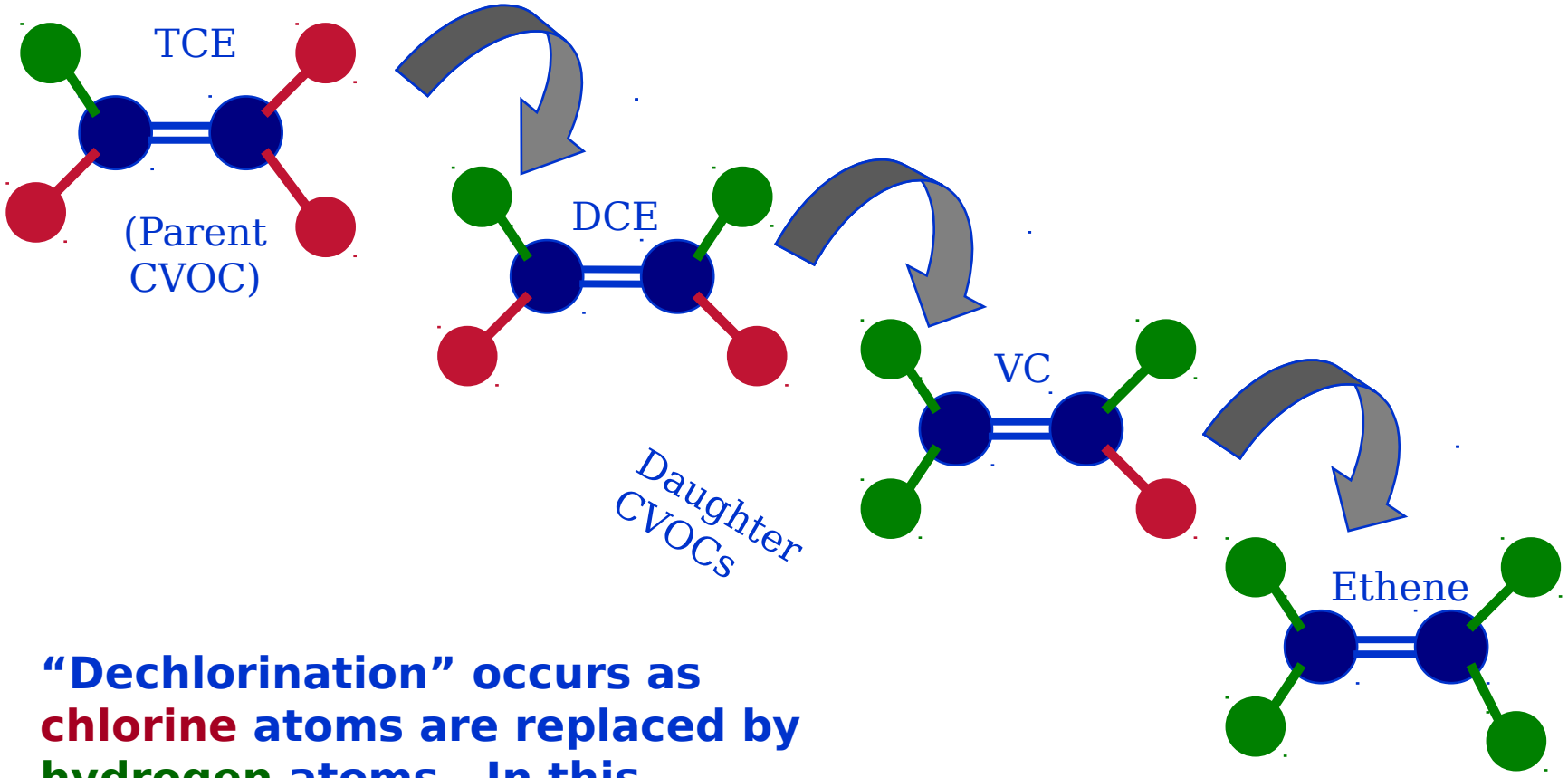
- **A natural process that removes chlorine atoms from “chlorinated” organic molecules, sequentially transforming them into less chlorinated “daughter” products**
  - **Biological - bacteria convert chlorinated solvents into harmless chemicals as part of their normal life-cycle**
  - **Abiotic - reactions between solvents and naturally occurring minerals eliminate chlorine atoms**

# Site Conditions Required for Reductive Dechlorination

- **Biologically mediated dechlorination of solvents works best under certain subsurface site conditions**
  - **Anaerobic (low oxygen)**
  - **Reducing (low redox potential)**
  - **Neutral pH**
  - **Moderate temperature**
  - **The right microbial populations**
  - **A sufficient organic carbon source (substrate, electron donor source)**



# Transformation of Chlorinated Ethenes




**“Dechlorination” occurs as chlorine atoms are replaced by hydrogen atoms. In this example, the final daughter product, “ethene,” is harmless (fully dechlorinated)**

# Pros and Cons of Natural Attenuation

## PROS

- Minimal construction costs/site disruption
- Capitalizes on natural processes
- Reduces mass and can ultimately eliminate toxicity
- Can reach CVOCs inaccessible to engineered remedies
- Can control plume migration
- Complements other strategies (e.g., source removal, land use controls)
- Often the most cost-efficient option for chlorinated solvent cleanup

## CONS

- Requires proper site conditions for full dechlorination
- Cleanup may proceed slowly
- Can result in toxic intermediate daughter products (DCE, VC)
- May require enhancements to shorten cleanup time
- May require exposure controls
- Requires comprehensive long-term monitoring
- Biodegradation can mobilize undesirable metals in groundwater

# Wrap Up

Questions?

*Thank you for your attention!*